NEW R&D TRENDS IN EUROPE ON THIN-SILICON PHOTOVOLTAICS

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ABSTRACT: About 99% of the solar-cell world production for PV terrestrial applications is dominated by silicon, of whose share, about 80% corresponds to wafer technology. Experience has induced the conviction that silicon technology must keep this predominant position for the next 10 years. Progress in wafer technology is needed in the direction of increasing production and lowering costs of feedstock, mainly by investigating new growth processes leading to a cheaper silicon of an acceptable quality. The development of medium-thickness polycrystalline ribbon silicon and similar silicon-based materials is in the forefront of photovoltaic R&D. In parallel, the efforts on thin-film silicon technology must be concentrated on enhancing material quality by improving film crystallinity and simultaneously thickness and growth rate. New approaches for the preparation of silicon impose a convergence of two research lines traditionally separated. The European state of the art in thin silicon for PV is analysed and described. A successful European RTD strategy imposes the collaboration of public and private institutions both within the present Framework Programme, FP5, and even more in the coming FP6, by means of Networks of Excellence (NoE) and Integrated projects (IP) in order to create the so called *European Research Area* (ERA).

Keywords: Silicon-1: Thin Solar cells-2: Heterojunction-3.

1 INTRODUCTION

Photovoltaic conversion of solar energy is based on semiconductor electronics. Although materials such as GaAs, $CulnSe_2$ and CdTe may be without any doubt valid alternatives, still today the photovoltaic market is by far dominated by silicon. About 80% of the solar-cell world PV production for terrestrial applications has its origin in monocrystalline- (c-Si) and multicrystalline-silicon (mc-Si) wafer technology. Most of the remaining 20% market is dominated by thin- silicon (amorphous, microcrystalline, nanocrystalline, etc.) and by hybrid amorphous-crystalline solar cells (a-Si, μc-Si).

Experience has induced the conviction that silicon technology must dominate the PV market for the next 10 years. The cause of this predominant position is the combination of a number of factors, such as the maturity of silicon PV technologies, the good and well-known optoelectronic properties of the material, its availability, lack of toxicity, cost, chemical stability, etc.

During 2001 a total supply of 26 000 tons of silicon reached the electronic industry, of which around 15% were used to supply the PV market. Europe is a leader in the production of crystalline ingots and wafers for PV applications, through companies like Scanwafer, Deutsche Solar GmbH, PV Crystalox Solar AG, Solar World, etc. Crystalline-silicon (c-Si) wafer-based technology must evolve towards lower costs by implementing new material-fabrication processes and making wafers thinner [1]. On the other hand, silicon grown directly on low cost substrates is forced to progress in the direction of improving the optoelectronic properties of the material and its growth rate and consistently of making the cell active-layer thicker. Several efforts have been done since 1994 based on European projects dealt with different options concerning substrates (silicon ribbons, conductive and insulating ceramics) and deposition technologies (high- temperature chemical vapour deposition - CVD) and solution growth-SG [2].

Low-temperature CVD by RF, VHF plasma-enhanced and Hot-Wire CVD depicts at present an extraordinary diversification arisen from the original amorphous-silicon technology. This development has led far beyond the appearance of a new family of materials or devices, resulting in the emergence of a new technology with totally different features, new limitations and new possibilities.

The consequence of all this is a clear convergence of two families of research lines -one based on wafers, the other on the growth of silicon onto low-cost substrates- that have traditionally progressed quite independently. Synergy can come out of this mutual approximation, and may be the origin of important advances in next-generation PV.

2 BACKGROUND

For a long while, wafer and thin-film technologies have evolved as competing options, i.e. as if the solutions to the technical problems could have come out from only one of these two research lines. In the last few years, however, new possibilities have arisen on the basis of a number of technological approaches for the fabrication of inexpensive multicrystalline silicon, for the growth of polycrystalline silicon thin films on inexpensive substrates or for the deposition of high-quality microcrystalline-silicon thin films at competitive growth rates. Among these techniques and materials are: edge-defined film-fed growth (EFG), string ribbon silicon, Silicon Film™, dendritic web growth, RGS silicon foil preparation [3] molecular-beam graphoepitaxial growth (MBGE), solid-phase crystallisation (SPC), zone-melting recrystallisation (ZMR), plasma-spray silicon growth (PSSG), liquid-phase epitaxy (LPE) molecular-beam epitaxy (MBE), hot-wire CVD, VHF-PECVD and more [9,10]

Some of these approaches have evolved from wafer technology as possible ways to lower costs by producing solar-grade silicon *ad hoc* rather than consuming material initially devised for the microelectronics industry. As compared to CZ mono-c-Si the subordination to lowering costs leads to the following key features:

- Multicrystalline instead of monocrystalline silicon.
- Thinner active layers ($\sim 10^1$ instead of $\sim 10^2$ μm)

- A more efficient use of raw materials.

The rest of the above mentioned techniques arise from the need of the thin-film-silicon technology (basically PECVD, i.e. plasma-enhanced chemical vapour deposition) to overcome certain limitations (defect density, photostability and fabrication throughput). This leading force results in the following targets (taking standard amorphous silicon as the reference starting point):

- Increased crystallinity.
- Thicker active layer (~10^0-10^1 instead of ~10^{-1} μm).
- Higher growth rates.

A rough view at the guidelines of both tendencies leads to conclude that the following characteristics define the key silicon material in next-generation photovoltaics:

- Medium crystallinity (Multi- or polycrystalline silicon).
- Medium active-layer thickness, in the range from a few microns to a few tens of microns.
- High fabrication throughput, either by epitaxy, fast solidification of melted silicon, fast film growth from gaseous silicon sources or similar processes.

Whereas it is unclear whether this kind of material will be obtained from the evolution of wafer technology, from that of thin-film technology or even from hybrid approaches, the mutual convergence of these two research lines is more and more obvious. Furthermore, the characteristics of new materials impose new limitations to device technology, thus requiring innovative solutions.

For instance, the use of cheaper, non-highest-quality, absorbers involves the risk of degradation of minority-carrier lifetimes associated with high-temperature processes such as those used in conventional wafer technology for the formation of cell emitters. Additionally, the decrease in active-layer thickness demands a more accurate definition of the junction, and correspondingly, of emitter thickness. These requirements, added to other factors such as the search for automatic module-assembly approaches, the need to lower costs by simplifying technology and spending less energy, or the tendency to produce large-area devices, have led to the development of a new PV sub-field: that of silicon-heterojunction solar cells (Si HJ). The low-temperature processes (<250°C) of this technology are not only cost-effective by themselves, but also allow the use of low-cost substrates that cannot be annealed at high temperatures, such as silicon ribbon and thin c-Si grown on glass [5].

Silicon-heterojunction cells, basically made of a crystalline-silicon (mono- or multi-crystalline) wafer or ribbon absorber and one or two thin-film-silicon emitter(s), are an excellent example of technological convergence and represent a promising option in seeking breakthroughs in photovoltaics.

Key features of silicon-heterojunction technology are [4]:

- A very simple fabrication process.
- An important cost-reduction capability.
- Relatively high efficiencies, with a high potential for significant improvements.

Particularly remarkable is the work done by Sanyo, who have reported 21% efficiency on a solar cells of this kind (so-called HIT) [6] and have consequently attracted much attention from the international scientific community.

3 PRESENT RESEARCH LINES IN EUROPE

Figure 1 shows the market share in year 2001 among photovoltaic technologies for the different areas of the world. A rough analysis of these data reveals:

- Different priorities in the EU, the USA and Japan.
- An emerging activity on non-silicon thin film photovoltaics (CdTe and CIGS). CIGS initiatives are mainly led by European companies.
- A significant development of silicon-heterojunction devices, focused in Japan.
- More interest for ribbon silicon in Europe and USA than in Japan and other areas.

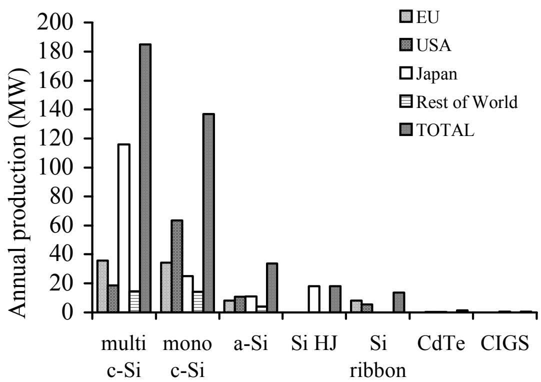

Figure 1: Annual PV production in year 2001 for the 6 most important technologies [7].

The market does not have a direct action on PV R&D, but this is enough to explain why the financial effort in Europe on basic R&D is relatively lower. Between 50% and 70% of the EU budget is not spent on long-term strategic R&D, but on PV demonstration projects [8].

In contrast to the well-defined and well-funded Japanese PV programme, the situation in Europe is characterised by a strong diversity in national programmes, some of which are individually strong, but with a high degree of fragmentation. On the other hand, a successful European RTD strategy imposes the collaboration of a large number of public and private institutions. In 5^{th} Framework Programme (FP), positive actions have been launched to increase collaboration and co-ordination via RTD projects, or Thematic Networks like *PV-NET* (Network for the development of a road map for PV R&D- http://www.pv-net.net), *PV-EC-NET* (Network for the co-ordination of European and national RTD programmes for PV Solar Energy-http://www.pv-ec-net.net) and, of particular relevance for silicon, *aSiNet*, (European Network on amorphous-silicon device technology-http://www.asi-net.net) .

These initiatives have the chance to become much more ambitious in FP6, via Networks of Excellence (NoE) and Integrated projects (IP). An Expression of interest has been sent to the European Commission under the acronym DepSil (NoE on Deposited Silicon). This

EoI, supported by 38 groups covering basically the whole spectrum of European organisations and companies involved in deposited silicon, in combination with similar actions in complementary areas, is pointed to make a significant contribution to the creation of the so-called *European Research Area* (ERA) in an important field.

3.1 National programmes / projects on Thin-Silicon RTD.

The R&D activity of European research institutions on thin silicon concerns both material and device preparation and characterisation. The high level is well know all around the world, and is to be considered a result of national efforts rather than the effect of a European strategy or policy. Owing to the difficulty to synthesise so much information in a short paper, here are just some non-exhaustive highlights of the ongoing activity (given in alphabetical order of organisations):

• CEMOP / UNINOVA (P): 27 MHz, μc-Si:C, nc-Si:C and production of large-area cells (30x40 cm^2).

• CNR-IMIP (I): PECVD deposition of a-Si, μc-Si, SiC alloys; Er-doped silicon thin films; fully μc-Si thin films with very low H-content even at low temperatures; growth of μc-Si on plastic substrates; optimisation of c-Si/μc-Si heterojunction solar cells (η=15%)

• CNR-IMM (I): Si HJ using single and double microcrystalline / amorphous emitters (η=14%).

• ECN(NL): Processing of inorganic thin-film cells: development of methods to grow silicon films by plasma sprayed silicon on ceramics. Advanced surface and bulk passivation and silicon nitride anti-reflection. Development of special ceramic substrates for film silicon applications and "adapted" solar cell concepts.

• Fh-ISE (D): c-Si thin-film solar cells (high-temperature approach) on low-cost silicon and ceramics. Methods: Si-APCVD (using $SiHCl_3$ at ~1200°C), zone melting recrystallisation Reference cells: one-side contacting (Si thickness ~45μm) η=19.2% [15], direct epi (37μm) on p+-Cz: 17.6%,: Activity foreseen for the future: Transfer of results on reference cells to "realistic" substrates, scaling of the substrates / cells to 10x10cm^2. Bringing c-Si thin-film to a state where pilot production can begin.

• HMI (D): Deposition of amorphous and thin-film crystalline-silicon solar cells by PECVD and ECR-CVD; defect spectroscopy by optical, electrical and electron-spin resonance methods; seed-layer approach for a poly-Si thin solar cells on glass:metal-induced crystallization techniques for seed-layer formation, epitaxial growth a T<600°C by ion-assisted deposition techniques, low-temperature emitter technology. Solar cells using heterostructures such as a-Si:H / c-Si. Results: η=16.2% for a-Si:H(n)/c-Si (p) cells using FZ- cSi wafer [16]. Hall-mobility measurements, in-situ lifetime measurement during plasma process.

• IMEC (B): Cells produced using polycrystalline silicon layers with grain size in the range of 10 μm (η= 5 – 6.5%). Monocrystalline silicon layers transferred from silicon substrates to Al_2O_3 substrates. The process is optimised allowing lift-off transfer area of 100 cm^2. Use of cheap silicon substrate using an active layer of porous-silicon film without being lifted off from the silicon substrate. The approach has yielded monocrystalline and multicrystalline silcon solar cells with η>12% for an active-layer thickness below 10 μm.

• IMT (CH): micromorph cells and modules; thin-film silicon cells on plastic substrates; module technology upscaling; LPCVD ZnO; introduction of VHF-PECVD and of the micromorph tandem concept. Micromorph-cell stable efficiency 10.8%; micromorph minimodule stable efficiency 9.8% [9].

• IoP Prague (CZ) Development of materials for solar cells based on thin-film silicon; studies of local electronic properties by combined UHV STM/AFM in-situ tests; studies of defect states in thin-film silicon; electronic-transport characterisation of thin-film silicon; formulation of models for growth and charge transport in microcrystalline silicon.

• IPE (D): flexible solar cells, transfer of monocrystalline-silicon thin films (thickness 10-50 μm) to arbitrary substrates; direct deposition of a-Si:H on polymers at 70^{o}C; aSi/cSi heterojunction cells. Efficiency: transfer cells η=16.6% (45 μm thick on glass) [11], flexible a-Si:H cells on plastics η=5%.

• IPV-Jülich (D): full technology for 30x30 cm^2 tandem modules, η_{stab}=11.2% a-Si/mSi (1 cm^2). η_{init}=10.3% η_{stab}=8,9% [12].

• LPICM (F): study of plasma processes and growth of thin films through the use of in-house in situ diagnostic techniques such as UV-visible ellipsometry; Kelvin probe and Time Resolved Microwave Conductivity; stable single-junction p-i-n solar cells based on polymorphous silicon with efficiencies close to 10% [13]; simple dry process to passivate silicon wafers with a quality comparable to that achieved by using standard HF cleaning procedures.

• TNO (NL): encapsulation and interconnection of a-Si and c-Si cells.

• TU-Delft (NL): microcrystalline, protocrystalline Si and a-SiGe:H by PECVD and Expanding Thermal (Plasma ETP-CVD CVD; studies of defect-state distribution in a-Si:H and pc-Si:H, PECVD; single-junction a-Si:H solar cells η_{init}=10.3% (no back reflector); tandem a-Si:H/a-SiGe:H solar cell η_{init}=8.7% (no back reflector); R_d(i)=0.1-0.2 nm/s; ETP CVD: single junction a-Si:H solar cell η_{init}=6.7% (no back reflector), Rd(i)=0.85 nm/s.

• TU Eindhoven (NL): high deposition rate (>1nm/s) to obtain p-i-n cells (η_{fin}=8%).

• Univ. Barcelona (E): HWCVD microcrystalline p-type emitters, HWCVD microcrystalline cells at low temperature (<200ºC). Plans for next future: development of HIT structures with HWCVD-deposited emitters.

• Univ. Ljubljana (SL) and Rome (I) "La Sapienza": modelling and simulation together with characterisation of thin-film semiconductor materials and electronic devices; simulator with electrical model for heterostructures and with optical model for multilayer structures with smooth or rough interfaces

• Univ. Utrecht - Debye Institute (NL): development of deposition techniques and high-rate thin poly-Si film and microcrystalline Silicon by Hot-Wire CVD, low-temperature thin film triple junctions, large-area solar cells and modules.

Univ. Patras – Plasma Technology Laboratory (GR): Process development, Scale-up, plasma modelling,

characterization and control for high rate deposition of amorphous and microcrystalline silicon.
• UPC (E): a-SiCx thin-film (PECVD) and HWCVD Si for surface passivation.

The institution of authors of the present paper, who hold a mutual collaboration on several projects, do in turn develop the following thin silicon PV R&D activity:
• CIEMAT DER (E): applications of deposited silicon (amorphous, microcrystalline and hybrid silicon). PECVD of amorphous silicon at high growth rates. Dry etching and passivation of c-Si surfaces. Wide-bandgap, highly conductive emitters. Development of silicon p-i-n and HJ cells and position sensors.
• ENEA (I): CR Portici: amorphous silicon solar cells using a wide range of technological options (Si, SiN, SiC, SiGe, and a-Si multijunctions , Hot-Wire CVD and VHF-PECVD), laser-scribing full technological process for large-area modules 30 x 30 cm^2 [14], η_{init}=9.1%, NREL-tested, Tandem devices , η_{init}=9.5% small area cells deposited on aSi on stainless steel, seed layer by standard LPCVD for epitaxial growth of thick polysilicon films, Solid-Phase Crystallisation (SPC), and Laser-Induced Crystallisation (LIC), development of processes suitable for industrial applications (screen printing, TCO), passivation and dry / wet conditioning of silicon surfaces for a-Si / c-Si HJ technology (η=16% 1.26 cm^2). Cr Casaccia: cSi Technology, Laser doping, screen printed contacts. The authors are available for further information on ENEA and CIEMAT activity here not presented due to the limitation of length of the test.

Some relevant groups, such as the British ones (some of which were pioneers in thin-film silicon), and a number of other prestigious teams are not presented here due to no reliable data received at the time of writing this paper. Additionally, difficulties were found in receiving useful and complete information to describe the activities of the European PV companies involved in thin-film silicon PV, such as Akzo Nobel (NL), Free Energy Europe (NL), RWE Solar - Phototronics (D), Intersolar (UK), Duna Solar (H), and more recently Eurosolare (I), having a share of 25% in Pacific Solar, and Pirelli Labs, in joint venture with Enel Greenpower, to start to produce on or before the end of 2003 amorphous-silicon based modules. The origin could be ascribed, for the authors of this paper, to definition of their future strategy for Photovoltaics at present not considered useful to be indicated

3.2 EU-funded projects

In the 5th EU Framework Programme (1998-2002) the policy of PV RTD was concentrated only on one strong project on thin-silicon solar modules (DOIT), whereas the others regard reduction of wafer cost production, or hybrid technologies. The first target, involves wafer producers, located particularly in Sweden, Norway, Germany and several European RTD institutions with a long experience on c-Si (FhISE, ECN, IMEC, HMI, Konstanz Universtity, etc). The following projects can be noted:
• SPURT (ENK6-CT-2001-30006) Silicon Purification Technology For Solar Cells at Low Costs and Medium Scale; Jan. 2002 / Dic. 2003 (2.0 M€).
• SOLSILC (ERK6-CT-1999-00005 a direct route to produce solar grade silicon at low cost; March 2000 / Feb. 2003 (2.2 M€).
• RGSELLS (ENK6-CT2001-00574)- Cost Effective, High Throughput Ribbon-Growth-On-Substrate Solar Cell Technology: Jan. 2002 / Dec. 2003 (2.3 M€).
• FANTASI (ENK6-CT2001-00561) Fast and Novel Manufacturing Technologies for Thin Multicrystalline silicon Solar cells; Jan. 2002 / Dec. 2004 (3.7 M€).
• FAST (ERK6-CT2001-00529) Fast low thermal budget area system for high throughput solar cell production; Dec. 2001 / Dec. 2004 (3.0 M€).

Further details can be found in web site: http://www.cordis.lu.

Of particular relevance for the scope of this paper, focused on European thin-silicon RTD, is the DOIT project:
• DOIT (ENK5-CT2000-00321) Development of an optimised integrated thin-film silicon solar module. Jan. 2001 / Dec. 2003 (3.9 M€). Partners: (c) Plasma Technology Lab.-University of Patras, IMT-Neuchâtel, IPV-FZ Jülich GmbH, RWE Solar, LPICM-CNRS, IP Prague and Free Energy Europe. The aim of the project is the development of an innovative silicon thin film solar module, exhibiting a stabilised active-area efficiency of 11% on a 30x30-cm^2 substrate. The device consists of an amorphous-silicon / microcrystalline-silicon tandem solar cell (micromorph cell) prepared on a low-cost TCO-coated glass substrate. In view of industrial production, a deposition rate of at least 4 Å/s is to be achieved for the intrinsic layer of the μc-Si:H bottom cell (aiming at 10 Å/s). For this purpose both VHF and conventional RF regimes are used. The developments include module fabrication technology, extensive TCO evaluation, and efficient light trapping schemes while the partners make use of appropriate characterisation techniques and advanced plasma control tools as well as process and device modelling. Actual results include measured 11.2% stable efficiency on small area-single cells from 30x30 substrates, showing good structural and thickness homogeneity.

Other projects involving hybrid technologies are:
• MOPHET (ENK5-CT2001-00552) PV-Module Processing Based on Silicon Heterostructures. Partners: (c) Eurosolare, Scanwafer, RWE Solar, ENEA. CIEMAT and UNSW. The project concerns the development of a new process for the automatic assembling of photovoltaic modules. This process guarantees a higher production rate, the possibility to work with large solar cells and lower temperatures, and a minor stress for the cells compared to the present hand-soldered scheme. The latter point gives the opportunity to employ thin film heterostructures such as mc-Si/c-Si, a-Si/c-Si, TCO/c-Si, which Sanyo has demonstrated to be good structures for high efficiency cells (HIT cells). The project also contemplates a switch from the traditional p-type substrate to n-type one in order to eliminate degradation effects due to boron-oxygen pairs. The expectations are to achieve heterostructure cells with η>15% average efficiency with printed process and η=17% in pilot line with buried contact process.
• METEOR (ERK5-CT2001-00543) Metal-Induced Crystallisation and Epitaxial Deposition of thin Efficient and low-cost crystalline Solar cells. Jan. 2002 / Dec. 2004 (2.5 M€). Partners: (c) HMI, Katholieke Univ.

Leuven, Vienna Univ. of Tech., British Photovoltaics Ltd and IMEC The project proposes a novel two-step process : preparation of large-grained Si-seed layers on glass (HMI) and ceramics (IMEC) by metal-induced crystallisation (MIC) on which subsequently Si is epitaxially grown by ECR-CVD (low temperature path) and CVD (high-temperature path). Targeting at an efficiency of 12% these layers will be used to make efficient solar cells. It is planned to present a mini-module with η=10% by thr end of the project. This innovative approach could result in a crystalline-Si thin-film technology with a cost potential below 1 €/Wp.

• SUBARO (ERK6-CT1999-00014) Substrate- and Barrier-layer Optimisation for CVD-grown thin-film crystralline Si Solar cells Apr. 2000 / Mar. 2004; ~4.0 M€). Partners (c) IMEC, Bayer Ag; FH-ISe, TU-Delft; RWE Solar AG; ECN; ENEA; CNRS, N.C. Starck Gmbh; Shell Solar Energy B.U; Everest Coating. The project deals with the numerous possible options for thin-film crystalline-silicon solar cells (for substrate and barrier layer), the selection of a suitable low-cost substrate, compatible with Si-deposition by means of thermally-assisted CVD (and possibly a liquid-phase recrystallisation and the development of suitable barrier layers to prevent impurity diffusion from the low-cost substrate into the active layer and to optimise internal reflection. A 12% efficiency obtained by a two-side contacting technology is expected on a 30x30-cm^2 module made on the selected conductive substrate / barrier-layer combination. A lower value (η=10%) is expected on a 10x10-cm^2 module made on the selected insulating substrate / barrier-layer combination with a one-side contacting technology. A Technology roadmap, describing the timing and technological evolution for introduction of thin-film crystalline Si solar cells on the photovoltaic market and the assessment of a continuous high-throughput CVD-reactor, compatible with the requirements of the solar cell industry are expected.

• ADVOCATE (ENK6-CT2001-00562) Advanced dry Process for low-cost, thin Multicrystalline-Silicon Solar-cell Technology (Dec. 2001/ Dec. 2004 ~ 2.7 M€). partner: (c) IMEC, Photowatt, UItrecht Univ, others. The project focuses on the cost reduction of c-Si solar cells by using screen printing and plasma to remove all wet chemical and water rinsing processing, by using environmentally friendly multi-Si cell fabrication processes on all types of low-cost crystalline-silicon substrates (standard multi-Si, EMC multi-Si, silicon ribbons). The process will concern large area, thin (<100 μm) and fragile silicon wafers with a high throughput and a low breakage rate on automated production lines. A cell having η> 16% is expected on ultra-thin wafers, employed to reduce, on mid-term the cost down to 1 €/Wp.

4 CONCLUSIONS

A significant progress of PV in the near future can result only from new ideas enabling to overcome the bottlenecks of traditional technologies. Silicon dominates the present scenario and will probably dominate it for the next 10 years at least. Silicon-wafer technology is evolving towards cheaper and thinner absorber layers whereas thin-films tend to be better and thicker in order to enhance charge collection and optical absorption. The search for breakthroughs is bringing both technologies together. This situation may result in an important synergy that can be essential for the future of PV.

The situation of thin-silicon R&D in Europe has been analysed. In spite of an enormous potential, results are behind those obtained by the USA and particularly by Japan. A much better degree of co-ordination of national policies, together with a decided support at European level is essential for filling this gap. Thematic Networks in FP5 and hopefully in a much higher degree Networks of Excellence in FP6 may help achieve this necessary harmonisation. The silicon thin-film community is presently well-organised in aSiNet. This may be a good starting point for the creation of a European Network of Excellence on deposited silicon and other complementary materials and devices.

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